Clay-rock alteration experiments at 80°C in closed and open conditions: application to the waste storage

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In the framework of radioactive waste storage in geological formations, many investigations were carried out to characterize chemical properties of pore water at the field temperature (*e.g.*, 20°C). However, few studies were devoted to the modifications that temperature could induce on the chemical composition of pore water in the host-rock. Among the chemical parameters which are sensitive to temperature, the pH and $CO_{2(g)}$ partial pressure (*i.e.*, $p_{CO2(g)}$) are likely the most sensitive. These latter parameters could also strongly impact the mobility of radionuclides in geosphere. Under thermal gradient, many reactions would occur such as minerals dissolution-recrystallisation or organic matter degradation. The knowledge of geothermal systems in sedimentary contexts tends to prove that whatever the mineral or/and organic contribution, $p_{CO2(g)}$ is likely constrained by a mineralogical buffer combining carbonate mineral (calcite, dolomite), quartz or chalcedony and alumina-silicate phases (kaolinite, illite or Mg-chlorite) [1]. Hydrothermal alteration experiments were carried out with Callovo-Oxfordian clay-rock with the aim of characterizing the ultimate step of thermal alteration at 80°C, which is the temperature expected in the waste storage.

The experiments were performed in both open and closed systems where initial $p_{CO2(g)}$ values were fixed (*e.g.*, $p_{CO2(g)}$=0.4 atm.). High solid/solution ratios (1 to 3 kg/L) are chosen in order to favour neoformation of secondary mineral phases. Aqueous and gas phases were regularly extracted at temperature and fully analyzed. The evolution of clay mineralogy was also characterized using X-ray diffraction profile modeling of experimental patterns and Transmission Electron Microscopy. Then, results obtained for solution as well as for solids were interpreted and discussed in term of thermodynamic equilibrium achievement.

After 15 months of alteration in closed conditions at 80°C, the $p_{CO2(g)}$ is stabilized at 1 atm. and final solution is equilibrated with respect to quartz, kaolinite, calcite and ordered-dolomite. Modeling of experimental X-ray diffraction patterns [2] evidenced a slight increase of the illitic layers content in mixed-layer minerals (*i.e.*, 5%). However, it is not possible to conclude to illite neoformation. Consequently, in absence of equilibrium with a secondary Al-Si mineral phase which would participate to the complete mineralogical buffer, the constrain on $CO_{2(g)}$ is not evidenced in these experimental conditions. Other experiments devoted for determining reaction pathways are currently in progress.

[1] Coudrain-Ribstein, Gouze & De Marsily (1998) *Chem. Geol.*, **145**, *73-89*. [2] Ferrage, Vidal, Mosser-Rück, Cathelineau & Cuadros (2011) *Am. Min.* **96**, 207-223.

Can submarine groundwater discharge balance the oceanic strontium isotope budget?

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It is not clear if the strontium (Sr) isotope budget of the modern ocean is at steady state [1]. It has been hypothesized that submarine groundwater discharge (SGD) is an important Sr source to the ocean [2], but few data exist for Sr in coastal groundwater or in the geochemically-dynamic subterranean estuary (STE). We examined Sr concentrations and isotope ratios from 9 globally-distributed coastal sites, and examined the behavior of Sr in the STE.

Dissolved Sr generally exhibited conservative mixing behavior in the STE, although large differences were observed in the meteoric groundwater endmember among sites (0.1 – 24 μM Sr). Differences in groundwater Sr concentrations and isotope ratios ($^{87/86}$Sr = 0.707-0.710) reflected aquifer lithology characteristics. In part, because groundwater Sr concentrations are orders of magnitude higher in less-radiogenic carbonate and volcanic island aquifers, the SGD endmember Sr ratio must be lower than modern seawater (i.e., less than 0.70916). A simple lithological model was used to estimate a global average groundwater endmember of 2.9 μM Sr with $^{87/86}$Sr = 0.7089, representing a meteoric-SGD-driven Sr input to the ocean of 0.7-2.8 × 10^{10} mol Sr a^{-1}. Meteoric SGD therefore accounts for 2-8% of the oceanic Sr isotope budget, comparable to other known source terms, but insufficient to balance the remaining budget.

Sr isotope exchange was observed in the STE at five of the sites studied, invariably favored the meteoric groundwater endmember signature, and reached up to 40% exchange at salinity 10. Using reported estimates for brackish SGD, the estimated volume discharge at salinity 10 (7-11 × 10^{15} L a^{-1}) was used to evaluate the impact of isotope exchange in the STE on the brackish SGD Sr flux. A moderate estimate of 25% isotope exchange in the STE gives a resultant SGD Sr endmember isotope composition of 0.7091. The brackish SGD Sr flux accounts for 12-25% of the marine Sr isotope budget, and does not appear sufficient to balance some 40% of the remainder.

Substantial uncertainties remain for estimating the SGD source of Sr to the global ocean, such as the volume flux of meteoric SGD, and lacking measurements of groundwater Sr isotope composition in major SGD regions such as Papua New Guinea, the South America west coast, and West Africa. Nevertheless, the combined sources of meteoric SGD and isotope exchange in the STE are a major component of the modern oceanic Sr isotope budget, and represent a Sr source to the ocean that may have contributed to documented fluctuations in the oceanic $^{87/86}$Sr ratio over geologic time.

[1] Davis *et al.* (2003) *EPSL* **211**, 173-187.
[2] Allègre *et al.* (2010) *EPSL* **292**, 51-56.